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The Influence of Chemical Interactions and Morphology on Transport Phenomena in Polymer Electrolytes

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Themes of This Talk

Water uptake and transport properties for polyaromatic membranes

- Strong dependence on IEC
- Connectivity of ionic domains important

Comparison of polyaromatic with Nafion® based membranes

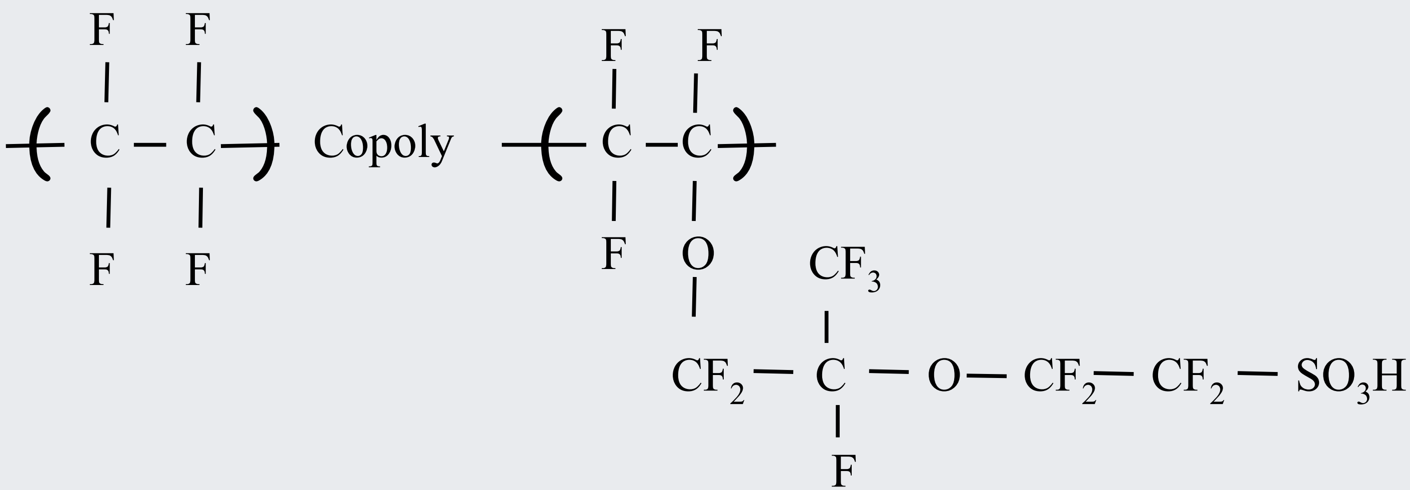
- Substantial differences at low water contents
- Both chemical and morphological differences apparent

Looking at transport at various length scales to reveal controlling effects

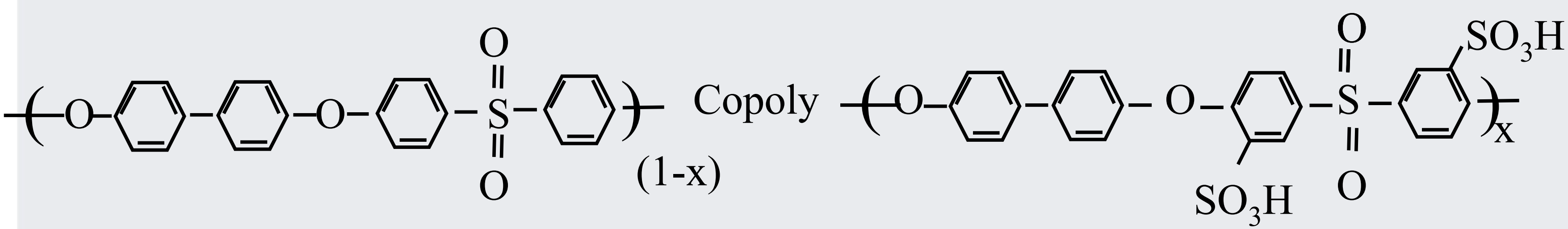
- NMR is the primary tool

Polymers Studied

Nafion



BPSH-X



F. Wang, et al., *Macromol. Symp.*, **175** (2001) 387-395

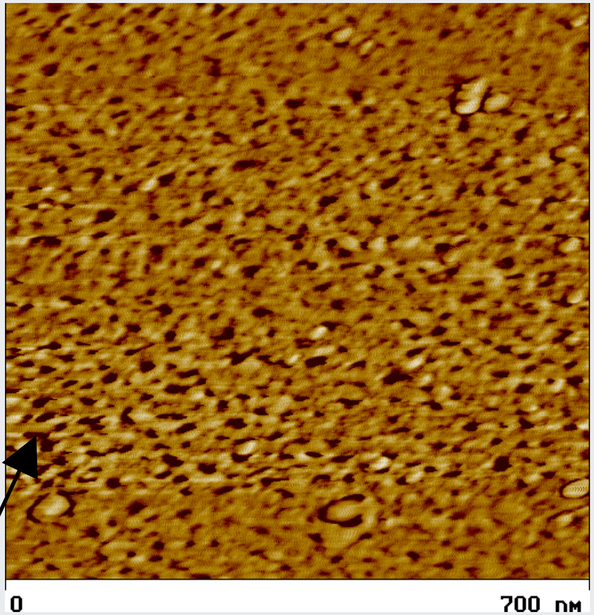
Characterization Methods: Focusing on Critical Information

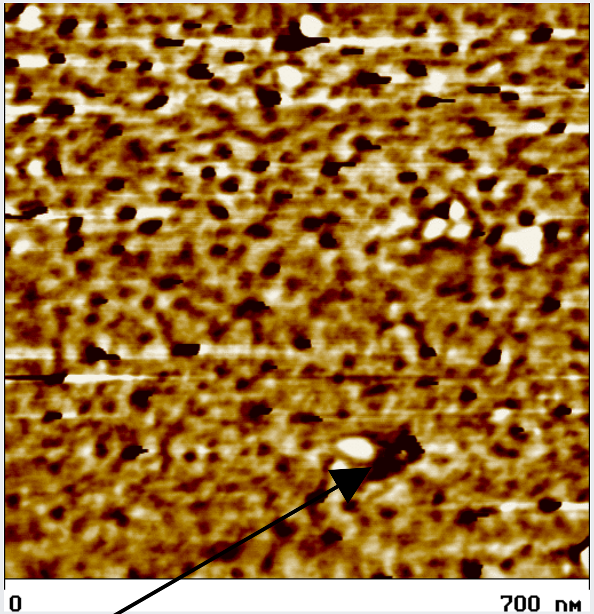
- NMR Methods explicitly designed to separate transport influences occurring at different length scales
  - 'Restricted Diffusion'
  - Comparison of Relaxation, Diffusion

- Spectroscopic Probes of water interaction with polymers, other components, each other

- Thermal Analysis to study strength of interaction between water and components and model compounds

AFM Images of BPSH





BPSH-20

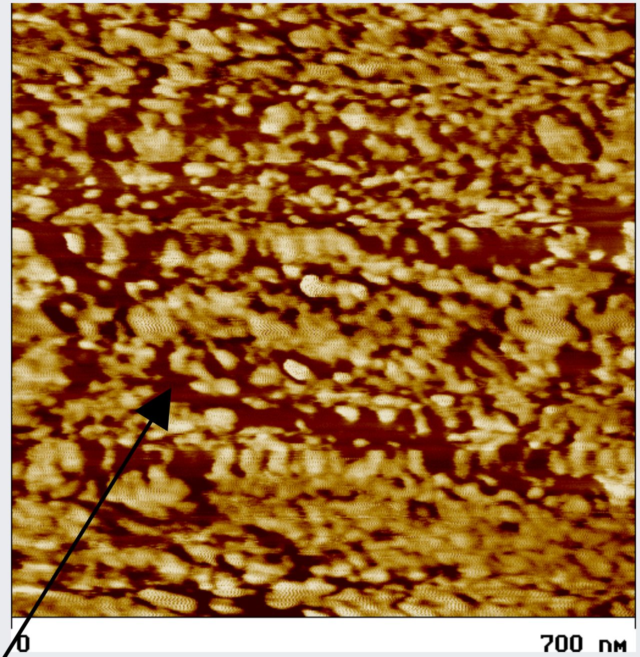
BPSH-40

Small, unconnected ionic domains

Larger domains, more connections

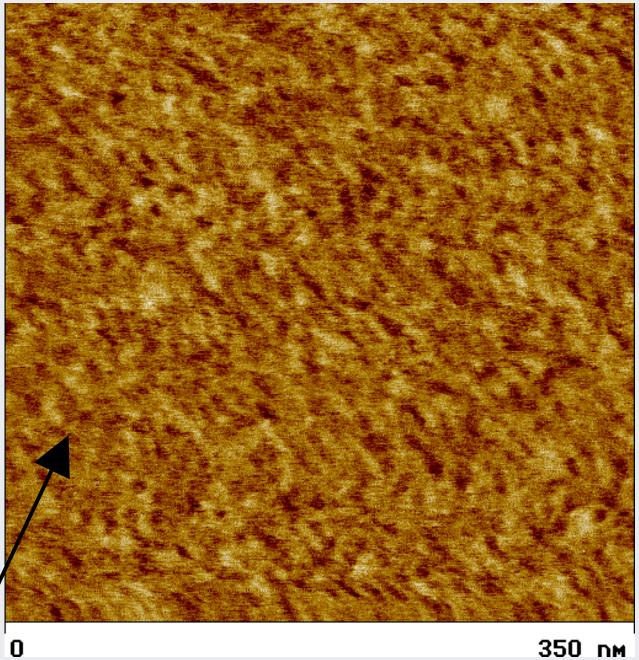
F. Wang, et al., *J. Membrane Science*, **197**, 231-242 (2002).

More AFM Images



Large, continuous ionic domains

BPSH-60



Small, well connected ionic domains

Nafion 117

NMR for mobility measurements

NMR T_1 Relaxation

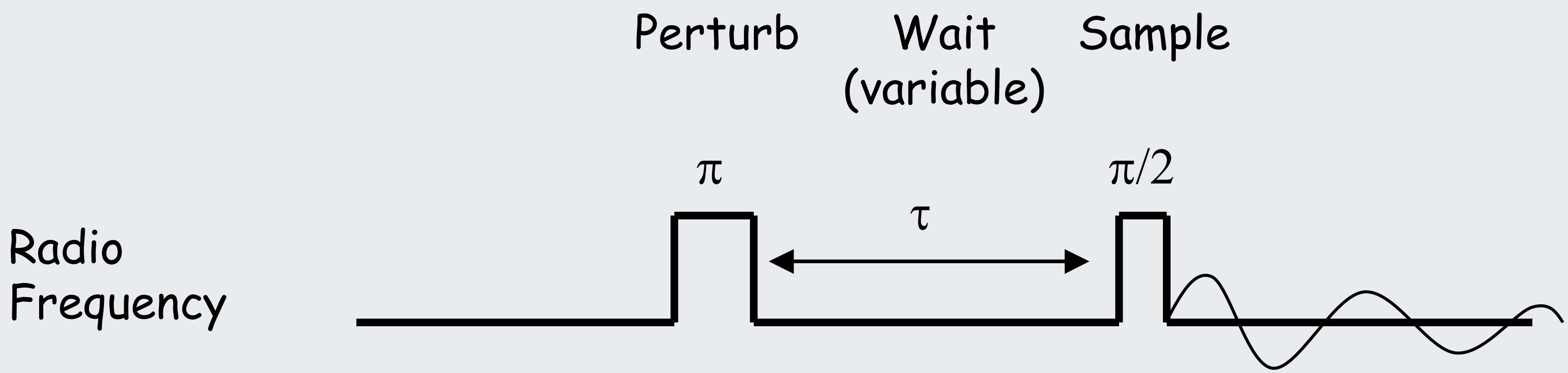
- Nanometer scale viscosity through Stokes Law
- Can be related to a diffusion coefficient
- Use D_2O for ease of interpretation
- Measures chemical effects between water and acid groups

NMR Stimulated Echo Diffusion

- Micron scale diffusion distances
- Use H_2O for SNR & signal attenuation
- Measures morphological + chemical effects

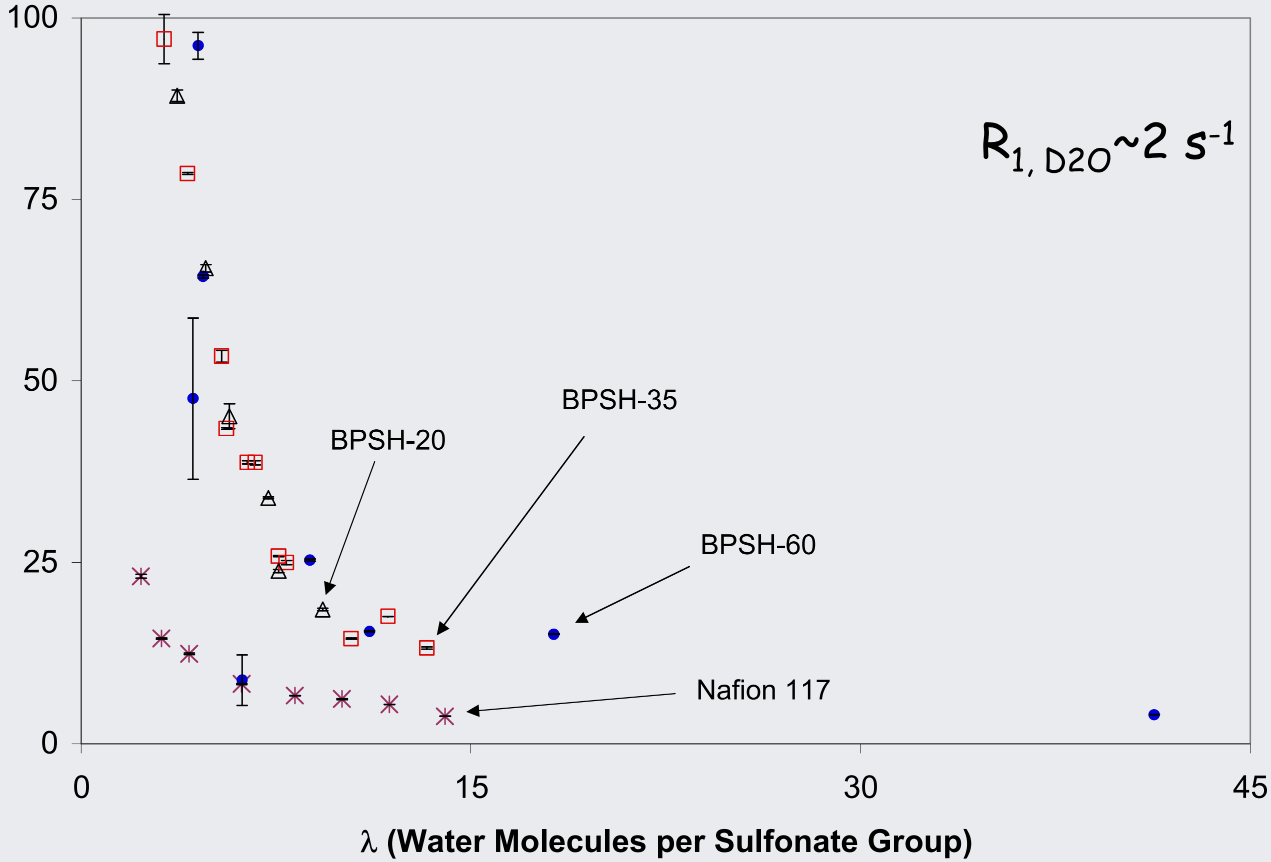
$\sqrt{2Dt}$

Measuring T_1: Inversion Recovery



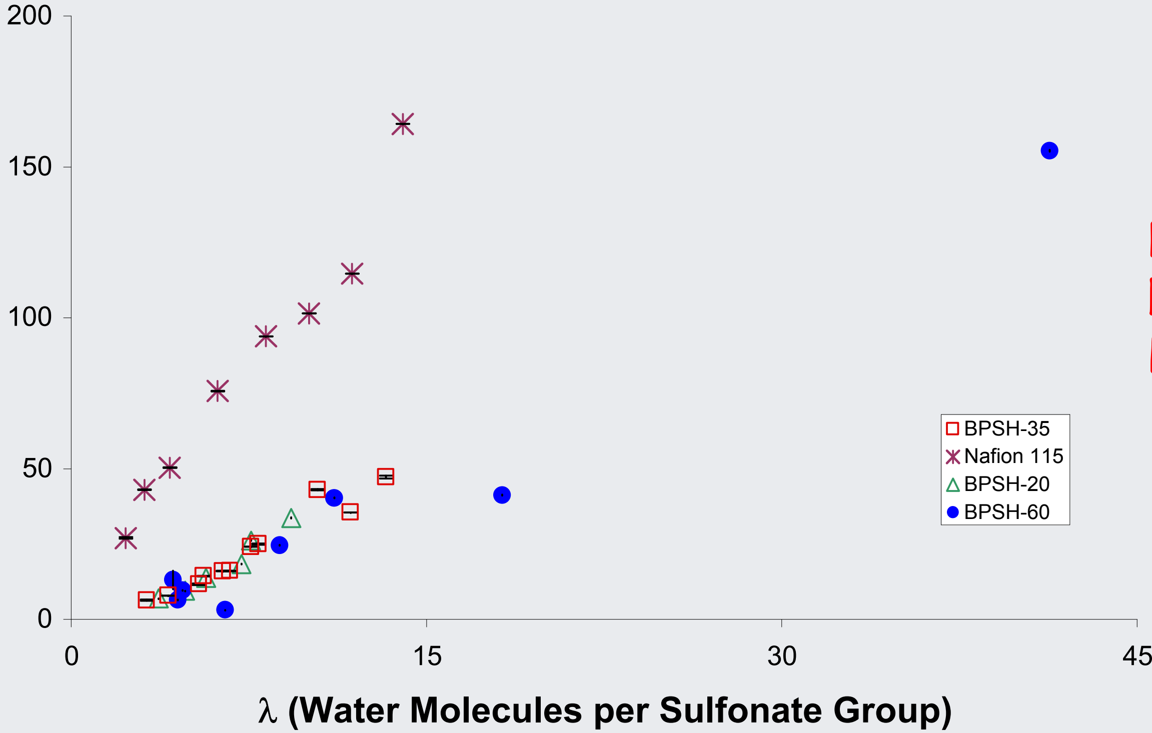
Vary τ, Fit to: $S(\tau) = S_0\ [1 - 2\exp(-\tau/T_1)]$

Deuterium Relaxation Rates for Water in Various Polymers



BPSH water higher micro- no, nano-viscosity → stronger interaction between water and fixed acid sites

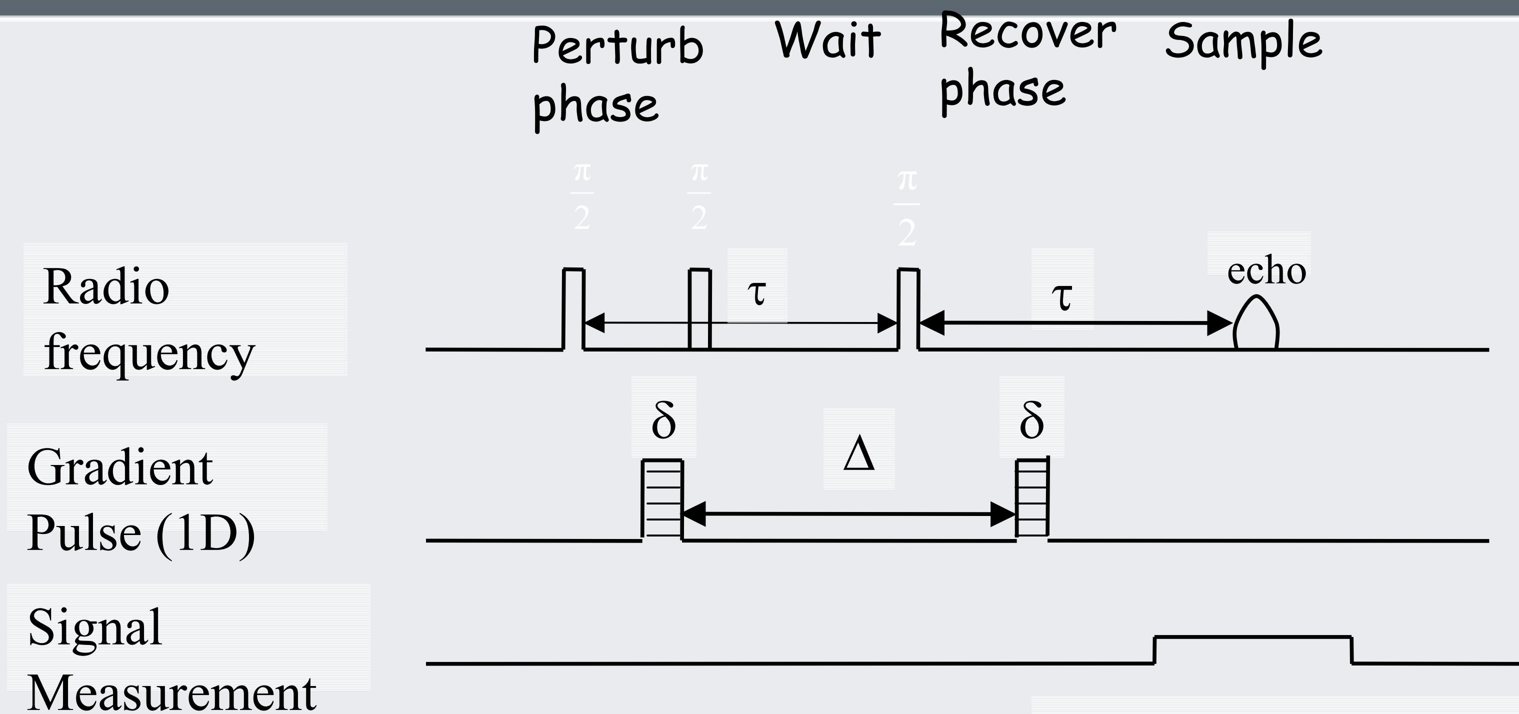
NMR Nano-Scale Diffusion from Relaxation



Dw in Nafion much higher than that in BPSH series

BPSH has the same nanometer scale motion regardless of the sulfonation level

Stimulated Echo Diffusion

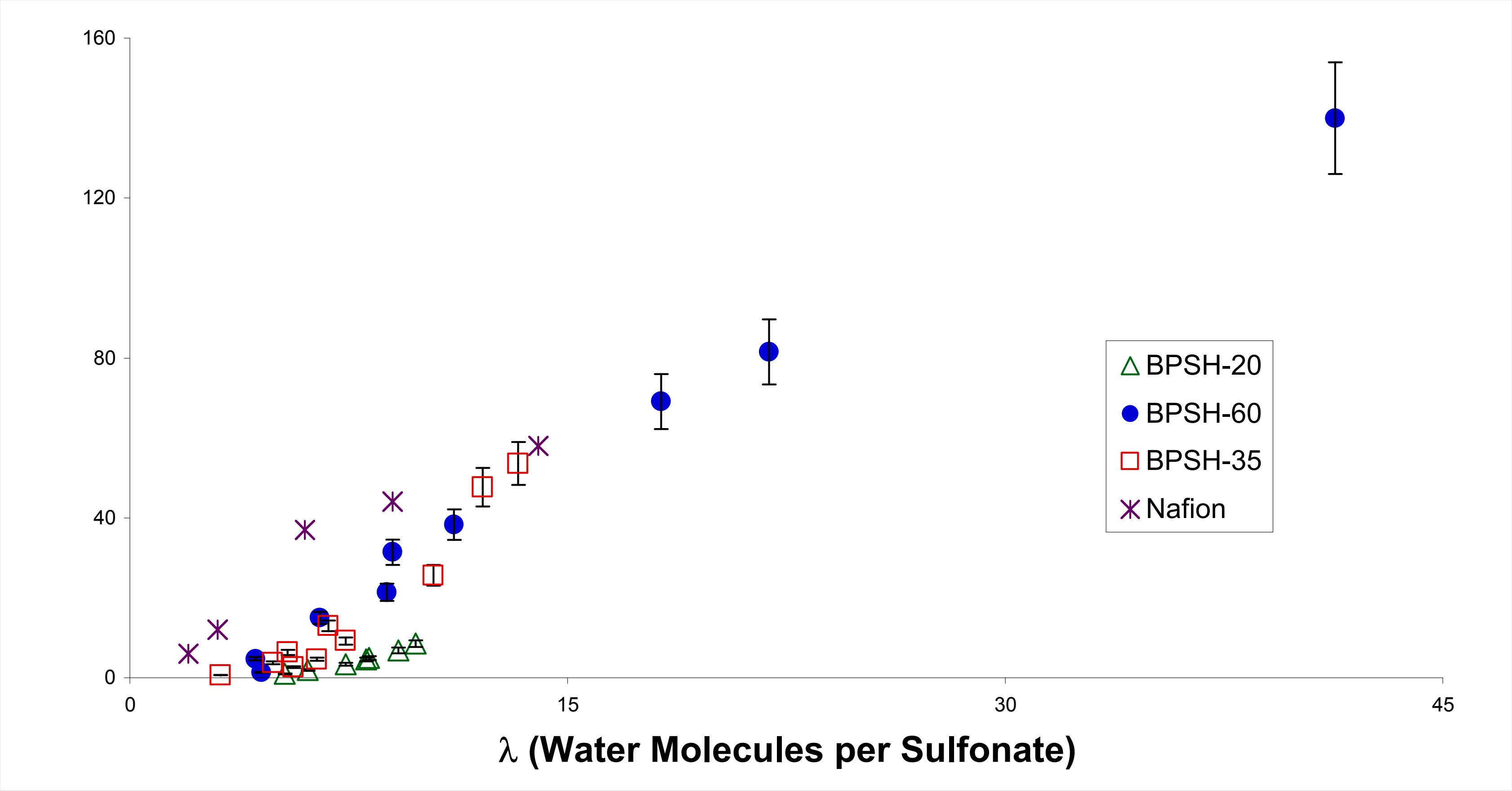


Δ = Diffusion Time

Vary g, Fit to: $\ln[\frac{S(g)}{S(0)}] = -\gamma^2 D g^2 \delta^2 (\Delta - \frac{\delta}{3})$

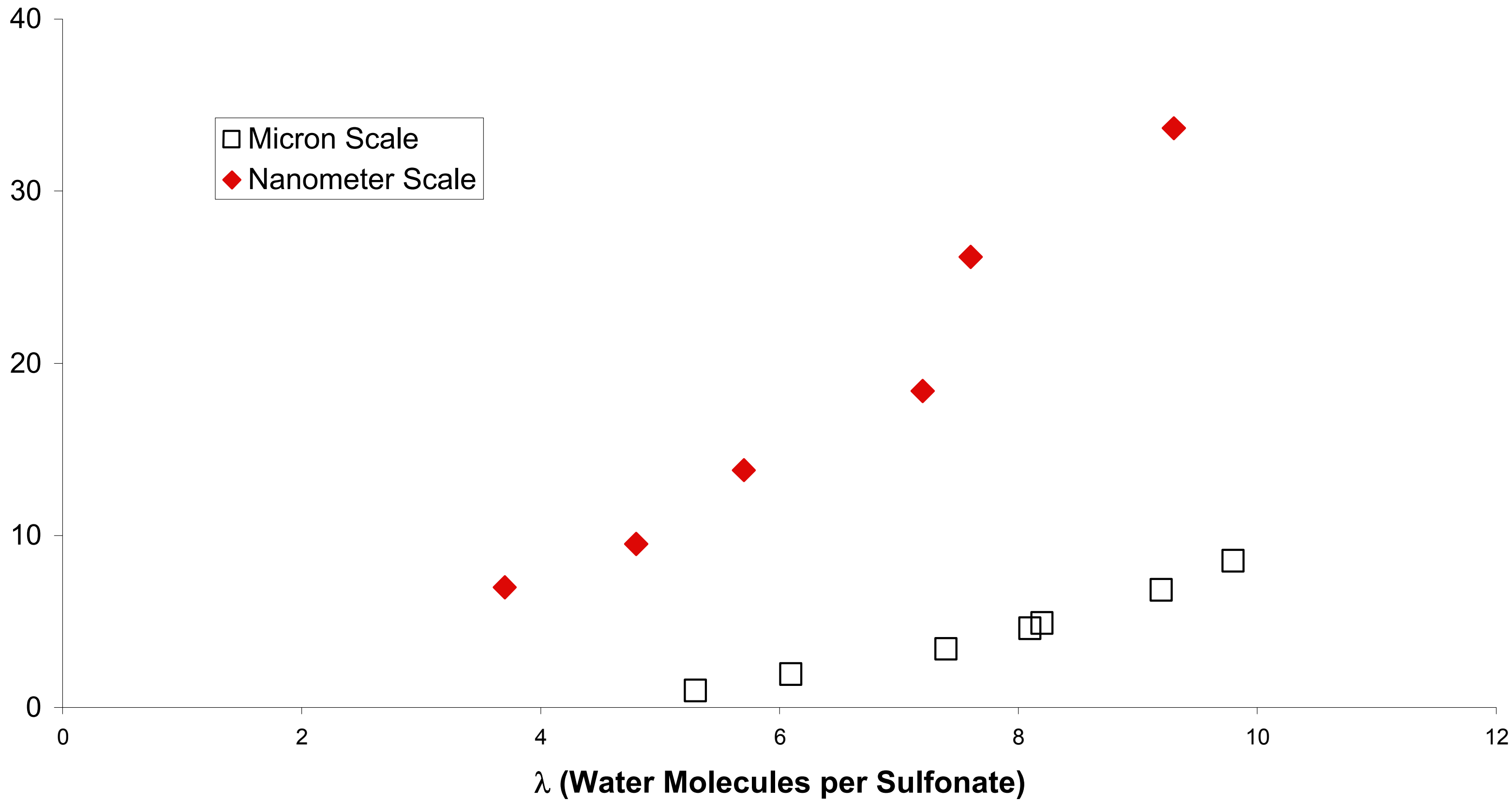
Self-Diffusion Coefficients

$D_w = 2.4 \times 10^{-5}\ cm^2/s$



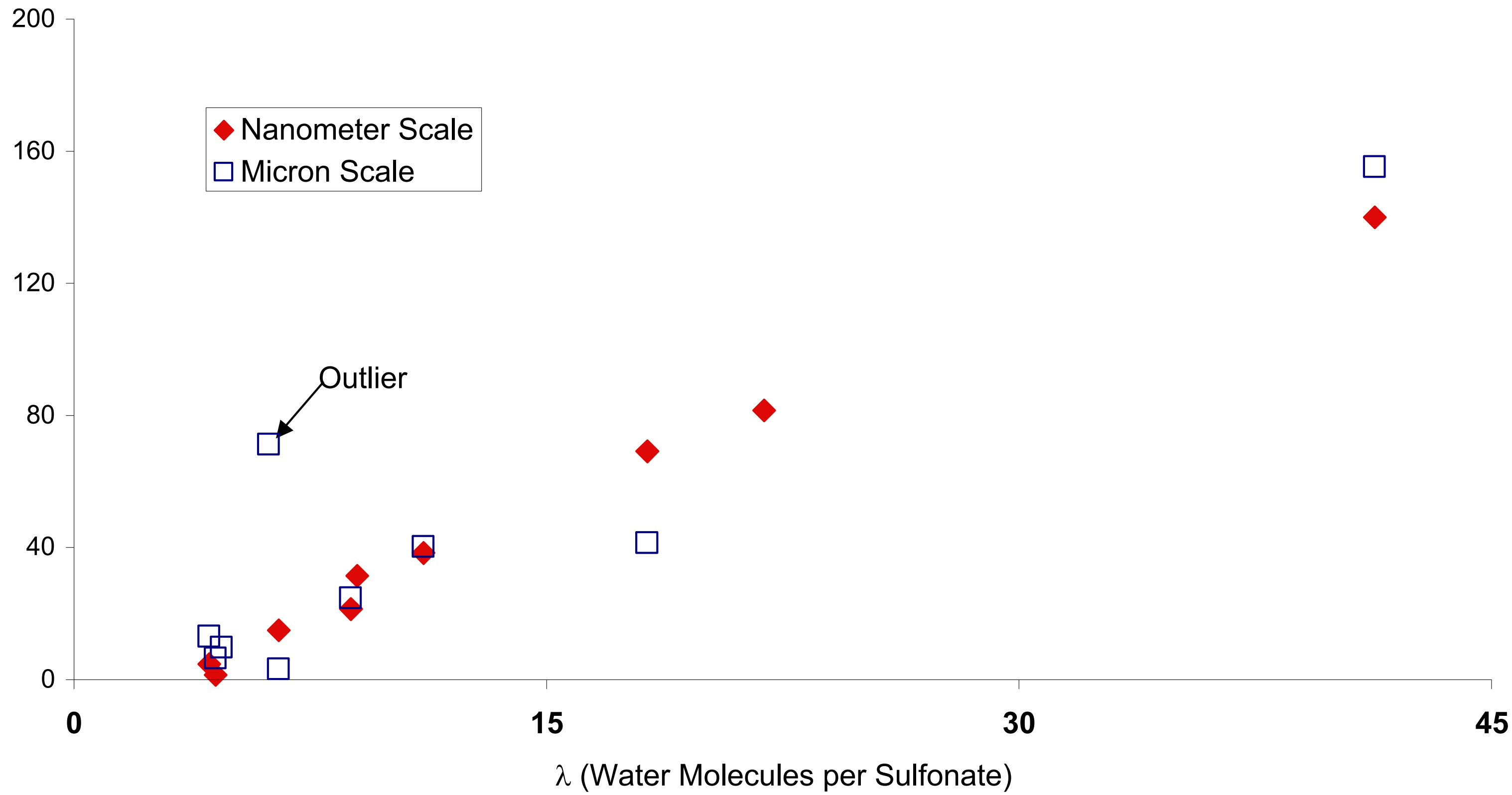
Nafion has much higher D at small λ.

Diffusion Length Scale Comparison, BPSH-20



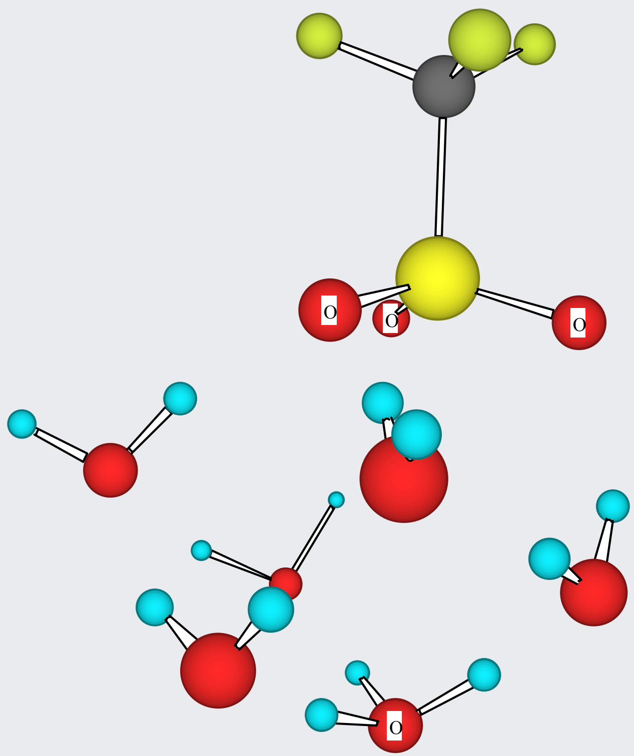
Diffusion coefficients diverge with increasing λ.

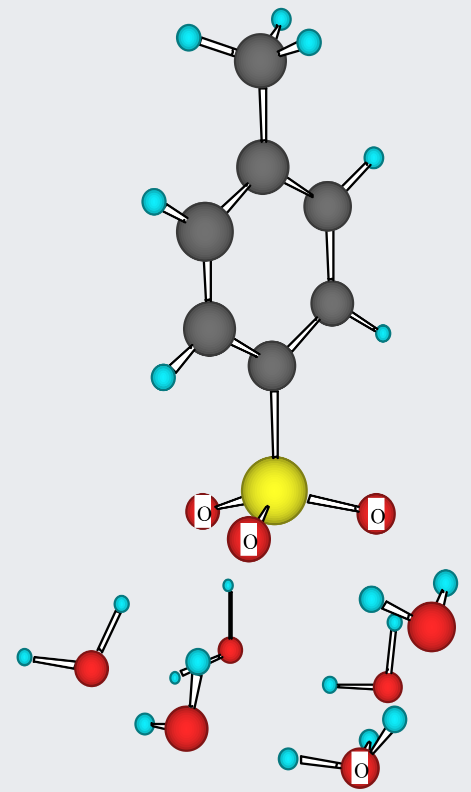
Diffusion Length Scale Comparison, BPSH-60



Similar trend and values over the entire λ range.

Conductivity Drops More Sharply w/RH for Ar-SO3H Why? Acidity of Different Groups...DFT Results





r(**O–O**)= 4.235 Å 3.914 Å

Summary of these Observations

Morphology strongly influences long range transport in BPSH-20, not in BPSH-60

Primary controlling factor in BPSH-60: local interactions between water and acid groups

Nafion vs BPSH: motion much slower at all length scales for equivalent water content

What are our Options?

- Increase Acidity of Functional Groups
- Increase Water Retention
- Provide 'Escape Route' for Protons from the vicinity of acid groups
  - High concentration of acid sites
  - Composite structures
  - Non-volatile liquid additives

- Our results suggest that morphology must also be carefully tailored